

A novel experimental method for obtaining multi-layered TiO₂ nanotubes through electrochemical anodizing

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Abstract In this study, a new parameter having influence on the TiO₂ nanotubes formation process is reported. Except of previously mentioned and well-known anodizing parameters such as voltage, time of anodizing, type of electrolyte, temperature, etc., samples' configuration in the electrochemical cell represents an important factor in the anodizing procedure. The electrochemical anodization is a group of interconnected processes and factors, each one of them having its specific weight on the final result. It was observed that the very short distance in between two titanium plates connected to the anodic terminal of the electrochemical cell is the decisive factor for creating superimposed TiO₂ nanotube layers. More precisely, it was found that the configuration of two parallel Ti plates being in close contact to each other, mounted to the anodic terminal and in parallel with the graphite cathode, favors the formation through electrolysis of multi-layered TiO₂ nanotubes. The microscopic observation of multi-layered TiO₂ nanotubes was performed through the removal of the upper layer of nanotubes using sonication. This peculiar result was interpreted using existed theories such as First

Fick's law and Nerst diffusion layer in combination with recently published research findings related to the effect of inter-electrode distance.

Keywords Anodizing titanium · Multi-layered TiO₂ nanotubes · Inter-electrode distance

1 Introduction

Titanium and titanium alloys are employed in several applications, due to their good mechanical [1, 2] and chemical [3] properties which allow for their surface modification [4–6] and nano-syntheses [7–10]. Between the various types of nanostructured titanium, the TiO₂ nanotubes became very popular in the scientific world. Owing to their uncommon nanotubular structure rendering some outstanding properties, TiO₂ nanotubes (also called titania nanotubes) arrays are proposed in applications such as: photocatalysis [11], gas sensors [12], photo-electrochemistry [13], dye-sensitized solar cells [14–16], biomedical devices [17, 18], and as electrochromic material [19].

Various TiO₂ nanotubes manufacturing methods have been proposed in literature. Amongst them, the electrochemical anodizing is a low cost process, yet known to allow superior control upon the nanotubes dimensions [20–23] when compared to other methods which include the use of nanoporous alumina template [24–26], sol–gel processes [27, 28], or hydrothermal techniques [29, 30]. One of the last trends in the manufacturing of these nanotubes is to combine them with different substances in order to improve their properties and make them easier applicable [31, 32]. However, although too many efforts have been done, TiO₂ nanotubes are rarely applied in practice; this probably is due to the fact that their formation, as well as

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their behavior, is still being studied, thus leaving space for novelty in fundamental research areas [33, 34].

Morphologic investigations of TiO₂ nanotubes were generally concentrated on aspects related to their diameter and height [35–38]. TiO₂ nanotubes inner and outer structure was described by applying criteria as, for example, interior architecture: (a) U-shaped [39] and (b) conical-shaped [40] or number of layers forming their wall: (a) single- [41] and (b) multi-walled [42].

Usually titania nanotubes grow in mono-layer; although some efforts have already been done to this direction, the idea of growing them in superimposed layers remained to an initial stage. However, a double or multi-layered nano-architecture is an interesting target with respect to the application of the nanotube layer in photovoltaic cells, as well as in bioengineering areas. It is now well-recognized that a high-efficiency photoelectrode for DSSCs (dye-sensitized solar cells) requires not only a high surface area for the loading of large amounts of dye molecules but also a tailored microstructure for light harvesting and fast electron transport. For the formation of an efficient DSSC, photoanode materials with various morphologies such as nanoparticles, ordered meso-structured materials, 1D structured materials (nanorod, nanowire, and nanotube), multi-layered nanomaterials, etc., are needed. 1D nanostructures, including nanotubes, nanowires, and nanorods, offer significant opportunities to improve efficiencies of solar cells by facilitating photon absorption, electron transport, and electron collection [43]. Previous studies affirmed that the photons coming from solar energy hit the walls of the nanotube, thus increasing the returned amount of energy [44]. TiO₂ nanotube arrays, in comparison to nanoparticulate systems, have superior electron lifetimes and provide excellent pathways for electron percolation [45]. A double-layered nanotubes' substrate might improve the energetic activation and also the photoelectric effect.

In medical applications, a multiple substrate of nanotubes favors the human cells proliferation, accustomed to a stratified environment. Green et al. [46] reported long-time ago in a study that single-cultured cells generate stratified colonies that ultimately fuse and form a tissue. Due to the complexity inherent at the soft tissue-to-bone interface and the need to replace more than one type of tissues, stratified scaffold design is critical for interface tissue engineering. The multi-tissue transition from ligament to fibrocartilage and to bone at the insertion site poses significant challenges for interface tissue engineering as more than three distinct types of tissue are present. In addition to supporting the growth and differentiation of relevant cell types, the ideal scaffold for interface tissue engineering must direct heterotypic and homotypic cellular interactions while promoting the formation and maintenance of controlled matrix heterogeneity. Consequently, the scaffold should exhibit a gradient of

structural and material properties mimicking those of the native insertion zone [47]. A significant challenge in achieving extended graft functionality is engineering the biological fixation of these grafts with each other as well as with the host environment. Biological fixation will require re-establishment of the structure–function relationship inherent at the native soft tissue-to-bone interface on these tissue engineered grafts. To this end, strategic biomimicry must be incorporated into advanced scaffold design. To facilitate integration between distinct tissue types (e.g., bone with soft tissues such as cartilage, ligament, or tendon), a stratified or multi-phasic scaffold with distinct yet continuous tissue regions is required to pre-engineer the interface between bone and soft tissues [48].

The formation of multi-layered TiO₂ nanotubes through the electrochemical anodizing was not frequently mentioned in literature. However, multi-layered titania nanotube arrays were reported to form in two different electrolytes or by adjusting anodizing voltage. In the later case, a two-step anodizing by switching voltage from high to low can effectively grow high-aspect-ratio TiO₂ nanotube arrays. As high voltage is applied first and low voltage secondly, large diameter tubes form at the top and small diameter tubes form underneath [49, 50].

In this study, a newly developed method for the formation of double or multiple layered titania nanotubes is described. The working parameters and the results are detailed below.

2 Materials and methods

Titanium dioxide nanotube layers were manufactured through the electrochemical anodizing method. The titanium foil was provided by Alfa Aesar S. A. Massachusetts and cut into 3 × 3 cm² samples having 1 mm thickness, using laser technology.

Each sample was cleaned before the experiment to start, by following the steps below:

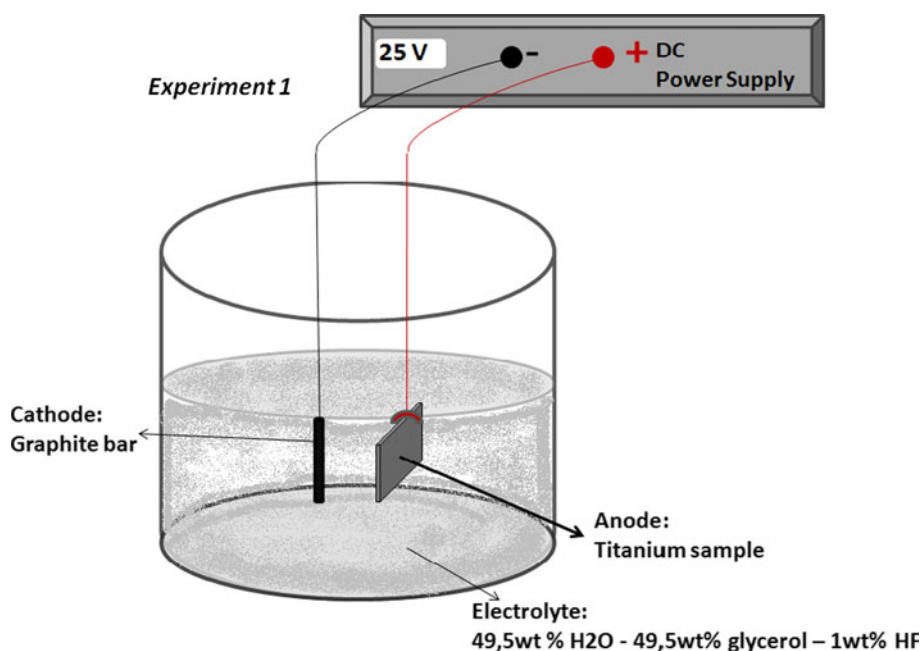
- The titanium sample was polished with sand paper (from 180 to 2,000 grit).
- The sample was sonicated in 50:50 ethanols–water solution, for 1 min at 20 kHz.
- The sample was cleaned in distilled water.

Two types of configuration were used for the experiments, as described below:

2.1 Experiment 1: One titanium sample was subjected to electrochemical anodizing

The electrochemical cell consisting of one power supply and two electrodes: pure graphitic cathode and one

Fig. 1 Scheme of anodizing conditions used in Experiment no. 1



titanium specimen serving as anode (see Fig. 1). The experiment continued for 8 h, at 25 V DC and in a 1 wt% hydrofluoric acid in 50:50 DI water and glycerol solution.

2.2 Experiment 2: Two titanium samples were subjected to electrochemical anodizing

The electrochemical cell was composed of a power supply and one pure graphitic cathode mounted in parallel with two titanium specimens in contact serving as anode (see Fig. 2). The separating distance in between the two samples was inexistent at macro scale level. The experiment continued for 8 h, at 25 V DC and in a 1 wt% hydrofluoric acid in 50:50 DI water and glycerol solution.

All experiments unrolled at room temperature. The anodized samples were exposed to sonication process for 4 min at 20 kHz, so that the nanotube layer to be partially removed. Afterwards, samples were left for drying and ulterior the TiO₂ nanotubes arrays were observed with a SEM device, Model Zeiss SUPRA 35VP, in the absence of any conductive sputtering. Samples involved in the “Experiment No. 2” were microscopically analyzed on both sides: the inner one—in the experiment, in direct contact with another titanium sample and, respectively, the exterior one—in the experiment, in direct contact with the electrolyte.

3 Theoretical considerations

By changing the electrochemical conditions during the anodizing process, for a range of valve metal oxides, multi-

layered structures can be growth. More precisely, a highly ordered and vertical layer synthesized under a parameter set may lead to a first geometry, and then underneath, a second layer of organized tubes can be developed with a different parameter set. The underneath layer can be initiated at the bottom of a tube (to break through the bottom of a tube), or in the space in between the tubes. Therefore, we can discuss about various types of super positioning.

3.1 Types of multi-layered TiO₂ nanotubes

When multi-layered nanotubes form an organized nano-architecture we speak about superimposed layers of nanotubes in which the upper level represents a projection of the basic one, as sketched in Fig. 3a. Very simplistic, the scheme shows each nanotube in the top layer standing on one nanotube of the basic layer. This way the nano-array lying underneath can be considered as foundation for the superior one; but their thickness and consistence are not the similar.

Another synthesis, reported by Chen and Lu [51] describes hierarchically branched titania nanotubes. The authors state that hierarchically branched TiO₂ nanotubes with tailored diameters and branch numbers are successfully achieved by adjusting the anodizing voltage. What it results is a multi-layer of nanotubes in which the basic layer has a number of nanotubes which doubles in the upper level, as represented in Fig. 3b.

It is interesting to note that an inverse of the previously mentioned effect was recently reported by Yang et al. [52] who synthesized the branched nanotubes in the inferior level, while the unification can be observed in the superior

Fig. 2 Scheme of anodizing conditions used in Experiment no. 2

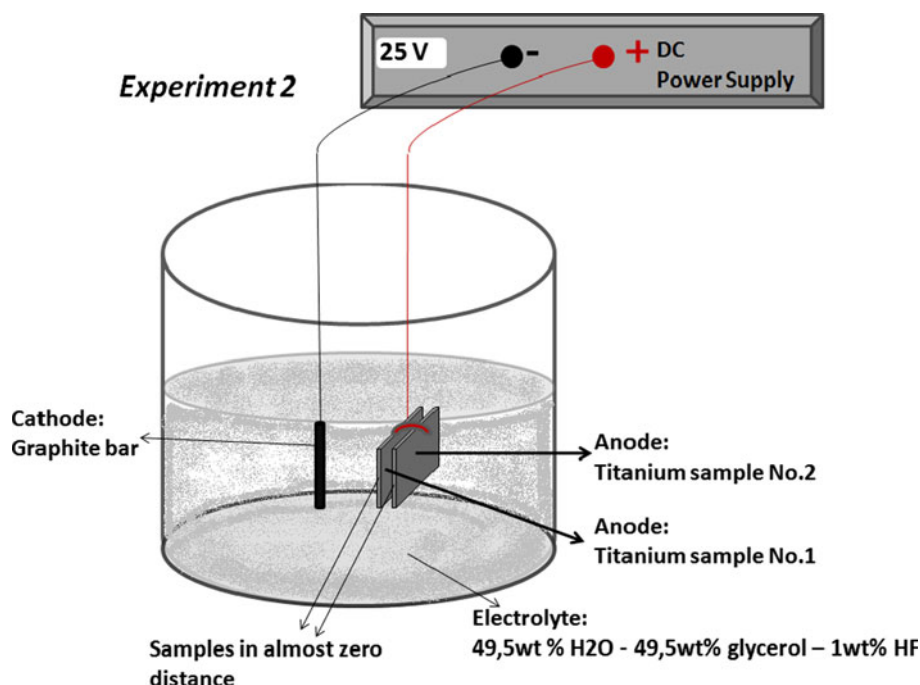
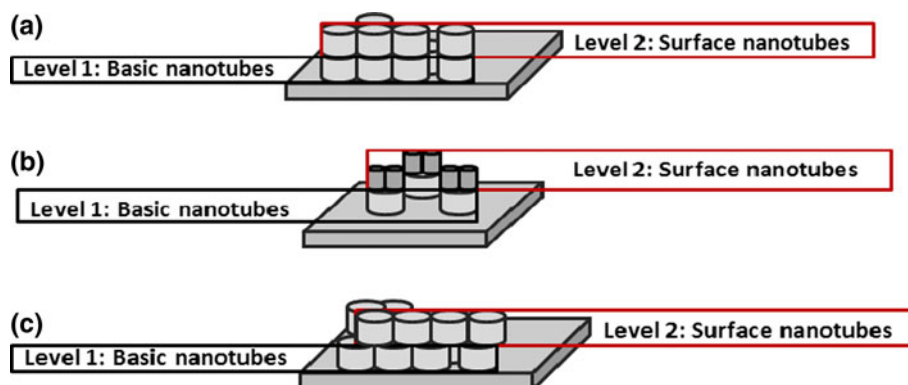


Fig. 3 **a** In an organized double-layer, nanotubes in Level 2 follow the pattern of Level 1. **b** Schematic representation for the formation of branched titania nanotubes. **c** Schematic representation for the formation of multi-layered TNTs



level. The main parameter responsible for this architecture is the temperature. Thus, we can observe how specific parameters set adjusted depending on the experiment lead to different results.

Finally, a possible multi-layered structure is composed by one basic layer covered by a second one while the later does not respect first's template. The placement of the nanotubes in the superior layer is considered random (Fig. 3c).

The nano-architectures presented in Fig. 3a, b can be synthesized by alternating parameters such as anodizing time, anodizing voltage, temperature, and electrolyte during the anodizing process; the manufacturing process of the multi-layer sketched in Fig. 3c is presented within the frame of this study and it was obtained through a different approach, respectively, by changing the number of

anodized titanium samples per experiment. For data interpretation the theory presented bellow has to be considered.

As mentioned before, the electrochemical circuit was assembled using a titanium anode and, respectively, graphite cathode. Typical electrolysis reaction involves the transfer of charge between an electrode and a species in solution. Due to the interfacial nature of the electron transfer reactions this whole process typically involves a series of steps. The mass transfer is usually achieved through (a) migration, (b) diffusion, and (d) convection. *Migration* is an electric field effect and depends upon the charge on the species, concentration and mobility in a field of force. *Diffusion* depends upon differences in concentration between species at the surface of the electrode and in the bulk solution. Finally *convection* arises from any mechanical or thermal disturbance in the solution.

3.2 Nernst diffusion layer

Nernst diffusion layer is a virtual layer, within which the gradient of the ion concentration is constant and equal to the true gradient at the electrode–electrolyte interface. The thickness of the Nernst diffusion layer may be measured on the graph “ion concentration vs. distance from the electrode surface”. Thickness of the Nernst diffusion layer varies within the range 0.1–0.001 mm depending on the intensity of convection caused by agitation of the electrodes or electrolyte.

According to the definition of the Nernst diffusion layer the concentration gradient may be determined as follows:

$$\left(\frac{\partial C}{\partial x}\right)_{x=0} = \frac{C_0 - C_c}{\delta_c} \quad (1)$$

where C_0 is the bulk concentration, C_c the concentration of the ions at the cathode surface, δ_c the thickness of the Nernst diffusion layer. Therefore the flux of ions toward the cathode surface is given by the relation:

$$J = D \frac{C_0 - C_c}{\delta_c} \quad (2)$$

Each ion possesses an electric charge. The density of the electric current formed by the moving ions is the following:

$$j = zFJ = zFD \frac{C_0 - C_c}{\delta_c} \quad (3)$$

where F is the Faraday's constant (96,485 Coulombs), z is the number of elementary charges transferred by each ion. The maximum flux of the ions may be achieved when $C_c = 0$ therefore the electric current density is limited by the value:

$$j_L = zFD \frac{C_0}{\delta_c} \quad (4)$$

The value of the limiting current density may be increased by increasing the bulk ions concentration C_0 .

3.3 Fick's laws

Diffusion is the mechanism by which components of a mixture are transported around the mixture by means of random molecular (Brownian) motion (cf. permeation: the ability of a diffusant to pass through a body, dependent on both the diffusion coefficient, D , and the solubility coefficient, S , i.e., permeability coefficient, $P = DS$). The flow of mass by diffusion (i.e., the flux), across a plane, is proportional to the concentration gradient of the diffusant across that plane [53–55]. According to First Fick's law, the diffusion of the ions through the layers controls the material transfer and the deposition rate:

$$J = -D \left(\frac{\partial C}{\partial x} \right)_{x=0} \quad (5)$$

where J is the flux of the ions in x direction, C the ion concentration as a function of x (the distance from the cathode surface), D the diffusion coefficient of the ions in the electrolyte.

Fick's second law predicts how diffusion causes the concentration to change with time; more precisely it states that the time rate of concentration change is related to the second derivative of the concentration gradient through the diffusion coefficient:

$$\frac{\partial C_x}{\partial t} = -\frac{\partial}{\partial x} \left[-D \frac{\partial C_x}{\partial x} \right] = D \frac{\partial^2 C_x}{\partial x^2} \quad (6)$$

where C_x the concentration at a distance x from the reference point, t is the time.

4 Results and discussion

Behind the utility of the experimental results interesting scientific explanations exist, related to the influence of the involved ionic species on the electrochemical processes that unroll, as well as on other electrochemical phenomena. For further understanding we describe in extent in the paragraphs below the results of the experiments.

Following the methods described in Sect. 2.1, surfaces of titanium covered by highly organized TiO₂ nanotubes were synthesized through the electrochemical anodizing method; results were presented in a previous publication [56]. A panoramic view of the nanotubes can be seen in Fig. 4a, while their lateral architecture can be observed in Fig. 4b.

In Fig. 4b, the titanium layer underneath the nanotubes is lightly corroded and no secondary layer of nanotubes can be seen. Nanotubes are carved in the titanium dioxide substrate, which is the main compound arising in the electrochemical cell as a consequence of unrolled chemical processes. When the layer of nanotubes is partially removed through sonication, the titanium surface remains almost flat. In the case of the “Experiment 1” the anodizing procedure takes place in a normal manner, without interferences or atypical phenomena. During the nanotubes formation process, within the cathodic diffusion layer the metal ion concentration non-linearly decreases toward the cathode surface. At the anode surface the metal is corroded and it dissolves in the electrolyte. As a consequence, the oxidation is produced and the titanium dioxide layer is formed.

The oxidation of titanium depends on the concentration and the diffusion of ions in the electrolyte. An important factor to this stage is the current intensity. An intense

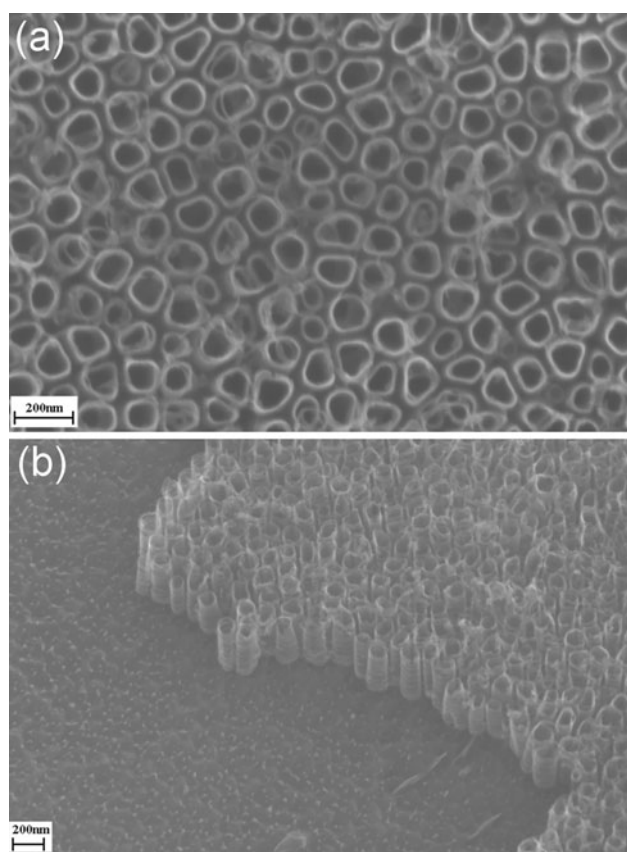


Fig. 4 **a** Panoramic view of TiO_2 nanotubes. **b** Lateral view of TiO_2 nanotubes

current determines the fast formation of titanium dioxide and the creation of large pores considered precursors of nanotubes. In this case, if the experiment runs for a long time at high voltage the nanotubes building up is followed by nanotubes shortening due to a continuous and intense corrosive activity. Corrosive phenomena continue inclusively after the titanium dioxide layer is entirely transformed into a titanium dioxide nanotubes layer. Thus, the corrosion is transferred to the top of the nanotubes affecting their height. In contrary, an appropriate current intensity and anodizing time lead to the carving of the titanium dioxide substrate, completed by a fast built up of nanotubes, meanwhile keeping a constant length increase. We have found the conditions used in “Experiment 1” as the preferential for the formation of highly ordered nanotube layers; it is important to mention that experiments were reproducible.

Applying the same experimental parameters, two titanium samples were simultaneously anodized for “Experiment 2”. The two titanium specimens were clipped to an anodic wire and mounted in parallel with the graphite cathode; they did not have a physical separation wall in between. After anodizing, samples were microscopically analyzed. SEM micrographs revealed the formation of

multiple layered TiO_2 nanotubes structures on the inner sides of the samples; limited areas of the bottom layer could be analyzed due to the applied ultrasonication technique which removed the upper level of the stratified nano-architecture.

The sonication procedure could not be controlled so that to assure a higher separation in between the superimposed nanotube layers. High sonication wave intensity applied for a long period of time determines the total removal of the stratified nano-structure from the titanium surface; for this reason the layers separation is restricted—in order to avoid the total damage of the nanotubes. The sonication time should be properly adjusted in order to partially conserve the nano-structure and meanwhile to enable the observation of a subordinated layer; in the present protocol the sonication time was of 4 min at a frequency of 20 kHz.

Some limited areas of the superimposed nanotube layers can be observed in the micrographs shown in Figs. 5a, b and 6a, b. Figure 5c offers an improved panoramic view of nanotubes developed in different plans. Nanotubes in upper level present enlarged diameter and they are well delimited, while the bottom ones are unclear and they present a dark shade. The pressure applied by the two titanium plates in contact and as a consequence the differences in ionic species existing in the electrolyte determined the appearance of non-uniform surface structure on areas of the samples. Areas of imperfections were formed on most samples as a result of improper electrolytic diffusion; such areas can be observed in Fig. 7

An important aspect in the electrochemical anodizing is the design of the electrochemical cell. In a study conducted on the electrolysis cell for iron production authors state that there is a need to be taken into account several considerations in order to lead to a process operated in conditions of minimum entropy production [57]. Those conditions enable uniform and steady rate for each of the unit-operations needed for a multi-phase process. Uniform current distribution supposes that the electrodes are rigorously parallel and of uniform electric potential. The related chemical engineering problems are firstly how to maintain close parallel surfaces with a uniform distance, and secondly how to supply a large amount of electrical charge to surfaces at a uniform potential. An infinitely small inter-electrode distance is impossible because of the need to allow growth of the deposit, to avoid electrical short circuiting and to avoid oxygen bubbles contacting the cathode. The necessary supply of reactant and of electrolyte flow requires a definite spacing between the electrodes.

On the other hand, an increase of the inter-electrode distance leads to a worsening of the current density distribution [58]. Studying the rates of electronic concentration and repulsion of fluorescein and fluorescently labeled DNA using a microfabricated biochip, Syrzycka et al. [59]

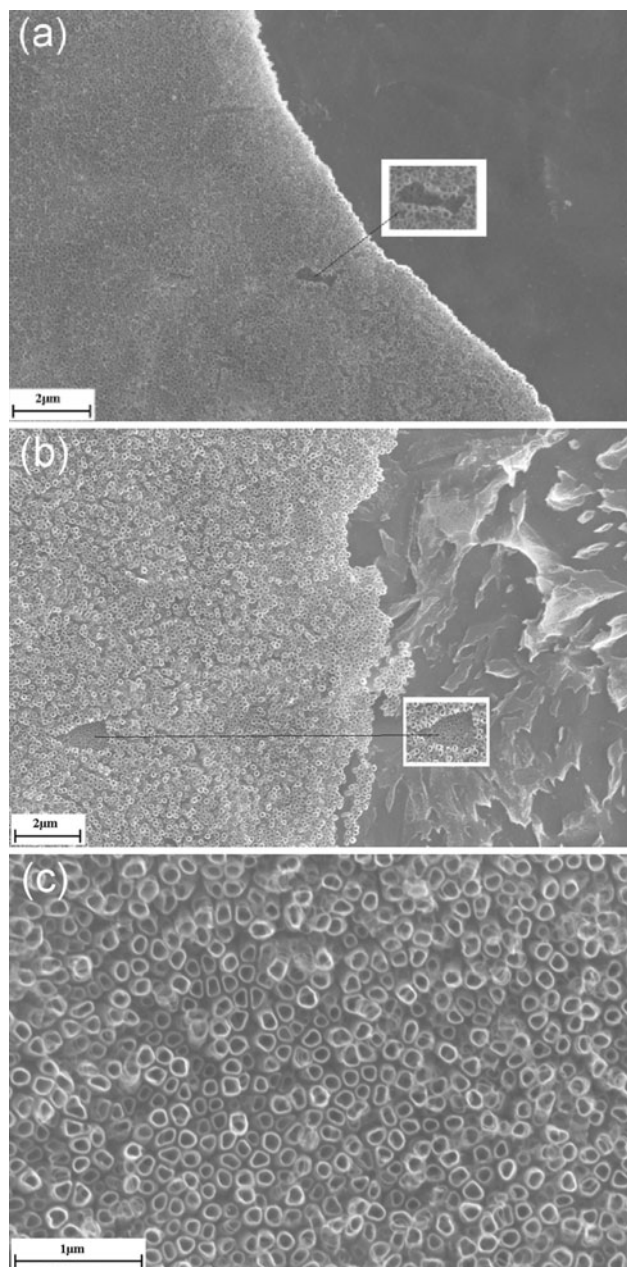


Fig. 5 a–c TiO_2 nanotubes arranged in layers on different levels

showed that doubling the distance between electrodes results in significantly lower concentration rates.

The limited inter-electrode space is considered a highly significant parameter in the synthesis of multi-layered nanotubes. As previously mentioned, multi-layered nanotubes were formed on the inner sides of the two samples, placed in contact on the duration of the experiment; on the exterior sides of the samples, coming in direct contact with the electrolyte, single-layer nanotubes were synthesized. This indicates that the distance in between the electrodes represents an important factor for the “multi-layer effect”. A simple explanation of the phenomenon could be that the

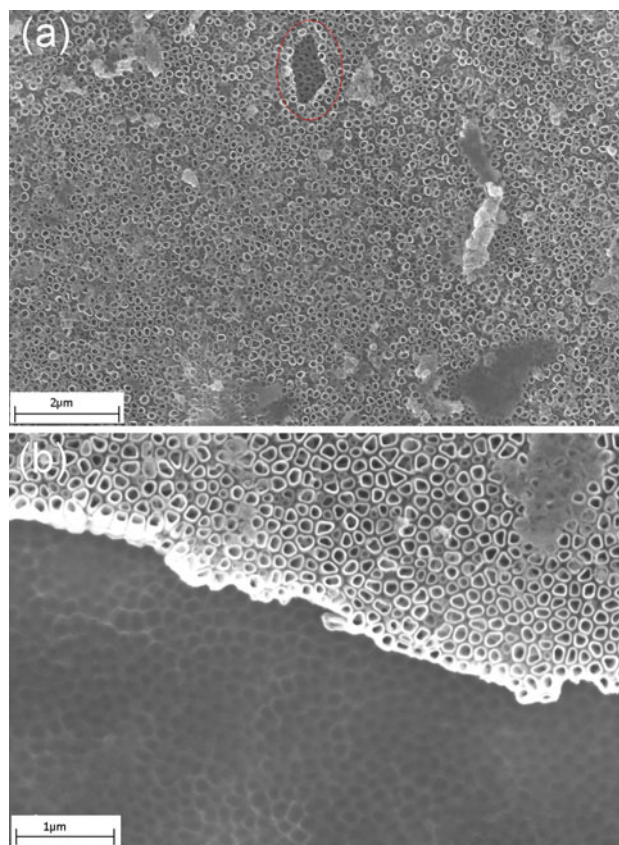


Fig. 6 a, b SEM Image-superimposed TiO_2 nanotubes layers

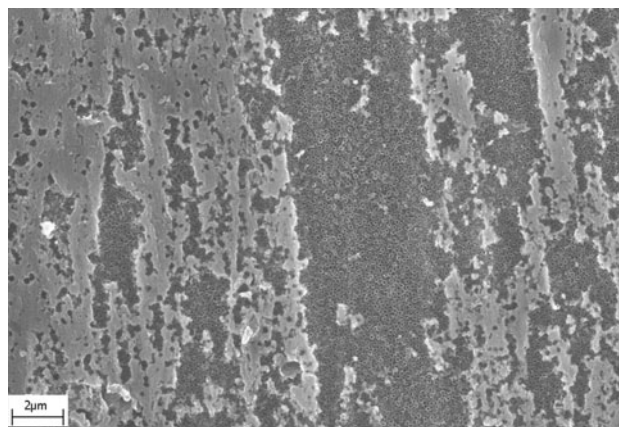


Fig. 7 TiO_2 nanotubes layer affected by inadequate electrolytic diffusion

double increased surface area of the titanium plate involved in the experiment and the pressure applied in between the samples in contact multiplied the ions concentration gradient in the electrolyte flowing in between the samples. However, a more advanced understanding is needed in order to explain why the effect on the two simultaneously anodized titanium samples consisted in the formation of a

stratified architecture of nanotubes, and not in a simple height and diameter increase of nanotubes.

The phenomena which determined the synthesis of multi-layered substrates of TiO_2 nanotubes are based on trivial, well-known concepts. A recurrence to some of these aspects assures a good understanding of the presented results.

In the electrochemical cell, electrolytic decomposition starts when dissolution of the substance starts and it is dependent on the existence of the electrical field producing the electrolysis, while the electrolysis voltage is strongly dependent on the current density, the conductivity of the water–wastewater to treat, the inter-electrode distance, and the surface state of electrodes [60]. In electrochemical reactions, the energy consumption is important for the feasibility of process development. For energy calculations, the cell voltage developed during the electrolysis is important and it can be reduced by keeping the electrodes at a particular distance [61]. Different morphologies of electrodeposited metal can appear at the different positions of the electrode surface.

The local current density during electrodeposition of a metal varies from point to point on an electrode surface. This is due to the following: the geometry of the system, the conductivity of the solution and electrodes, the activation overpotential, the diffusion overpotential, the hydrodynamics of the system. The current distribution on a macroprofile is very important in many electrochemical technologies and devices. In an electrolytic conductor it is the ions that move and carry the charge [62]. In the electrolyte, the ion transfer process results in formation of thin electrolyte regions (diffusion layers) adjacent to the electrodes where there are gradients of ion concentration. The concentration gradient is the main driving force behind electrolyte movement. The concentrations beyond the regions (bulk concentration) are constant with respect to the distance from the electrodes.

As mentioned in the previous paragraph, ions transport determines the concentration gradient in regions of the electrochemical cell, and this is directly connected to ions speed. Initially, the current generator exerts forces that accelerate ions speed. In time, due to friction, ions achieve a constant speed called limit speed and noted “ v_∞ ” which is equal to “ τ ”, the agility of ions movement, multiplied by “ ε ”, the intensity of the electrical field. The critical moments, when corrosive phenomena mold the nano stratified architecture are in the beginning of the electrolysis, when the fast ions motion at their maximum speed determine the creation of pores followed by the construction of the basic layer of nanotubes.

In the particular case of two simultaneously anodized titanium samples, both connected to the positive terminal of the circuit, their inner sides are affected by an increased

gradient of ion concentration. The cations concentration is obviously double as two titanium samples are involved in the experiment. In addition to the increased cations release, many other factors interfere in the evolution of the electrochemical processes. An important aspect is that these cations arising from titanium surfaces are trapped in between the two samples. Thus, in the area between the samples the oxidative processes follow a different course. In Fig. 8, we can see a representation of Nerst diffusion layer for two simultaneously anodized titanium specimens. The double increased cations number determines the increase of ions concentration C_0 in the bulk substance, while the concentration at cathode surface increases in initial stage, as the cations arrive transported by the current flow. According to first Fick’s law, ions diffusion coefficient D controls the material transfer; this depends on ions flux, ions speed, electrolyte viscosity, direction of ions, and inter-electrode distance. Second Fick’s law shows how concentration changes in time, therefore how reactions taking place during anodizing reverse the processes changing the parameters enumerated previously. In such a case we can admit that ions diffusion, expressed through first Fick’s law, characterizes the first part of the electrolysis and it depends on a set of parameters which determine specific chemical reactions; in a secondary stage of the electrolytic progress this phenomenon is reversed; as feed back, the arisen chemical reactions influence different parameters which cause the change in ions diffusion, this being expressed through second Fick’s law.

The increase in ions concentration accelerates the electrochemical processes and creates an extremely active network of ionic species, which is amplified in between the two titanium samples, as it is schemed in Fig. 9. When two titanium samples are so close to each other that they are actually in contact, corrosion and oxidation on their interior sides are acting aggressively, fastening nanotubes buildup. The alternative, rich in ionic species flows determine the repeated scallop of orifices which subsequently increase in height taking the shape of nanotubes, assembled in a stratified nano structure.

Any electrochemical circuit tends to be completed/ finalized through a global balance of the negative and positive species. In the initial moments, when the movement of ionic species suddenly starts and increases in zero time due to the current given to the circuit, the flux of ions is maximum; a competition between the positively and negatively charged particles is initiated in order to be reached the equilibrium state. The equilibrium occurs after all processes stabilize and when there is a fair diffusion of species in the electrolyte. To this contributes the electrolyte itself, containing the hydrofluoric molecules that directly enter into the electrochemical reactions which take place at the titanium surface. However, an important role plays also

Fig. 8 Scheme of Nernst diffusion layer for two anodized titanium samples

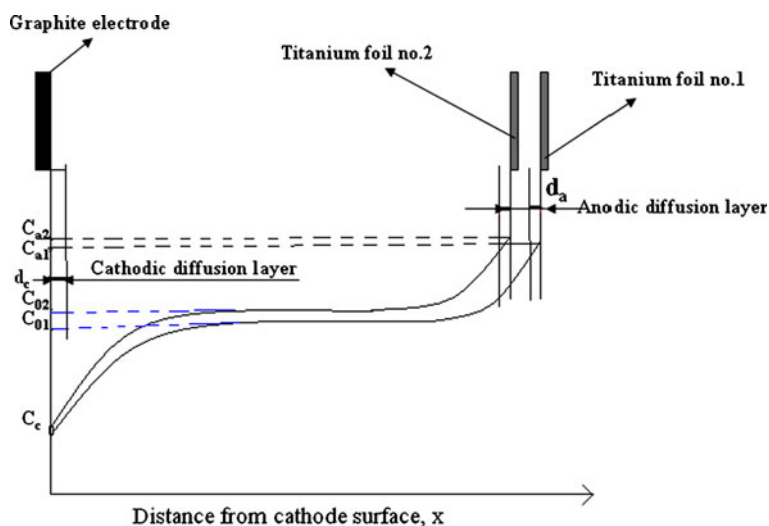
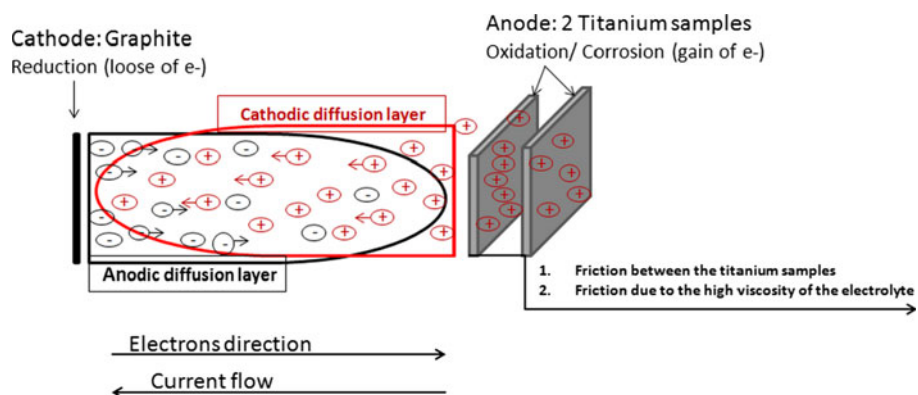


Fig. 9 Ions release and path in the electrochemical cell



the time. As time passes, the ionic concentration gradient changes due to the stabilization of reactions and mainly because of the distance taken by ions from the electrodes surface. Processes do not reach the same intensity on the whole duration of the anodizing procedure, but they are more intense in the initial part of the experiment. Considering this observation we conclude that the porous structure is formed during the initial period of the anodizing process, i.e., when the system shifts from a steady to an active state and leads to nanotubes formation in short time after this first stage.

During the electrochemical anodizing the motion of the electrolytic molecules, as well as ions flowing in the electrolyte and the given electric field create a continuous movement of the system, and determine the displacement of electrochemical activities. In this case, the delay in ions transportation is a result of friction between the organic molecules of the electrolyte, as well as between the two titanium samples positioned in contact. The corrosion and the buildup of nanotubes are not processes localized in a certain sample point, but their position change depending on the forces applied on the interior sides of the titanium samples. A careful analysis of Fig. 5b shows that titanium

substrate positioned under the layer of nanotubes is corroded at different sites and levels, while plateaus are created.

We have previously mentioned that one of the important factors affecting the quality of a deposit is the current density during anodizing. The effect of inter-electrode distance on the rate of metal deposition on a cathode determines the value of the current intensity and of many other parameters, strongly interconnected, and important for the complex electrochemical anodizing process. In a rectangular electrolytic cell with plane electrode parallel to each other and covering the end walls completely, the current density is in general the same at all points. The current lines are perpendicular to the electrodes in the same manner as the field lines in capacitors except near the edge. Under most practical conditions, however, a different geometry prevails and accordingly the current density is not uniform. Consequently, the current distribution in the electrolytic cell is determined by linear and non-linear dimensions such as breadth of electrodes, distance between cathode and anode, and distance between crests and troughs of profiled electrodes [63]. It is suggested that the almost inexistent distance between the two titanium

surfaces mounted to the anode is crucial for the formation of multi-layered nanotubes.

We shall underline that the uncovered by nanotubes area exposed in Fig. 5b was not immersed in the electrolyte during anodizing, therefore it was affected just by extensions of the electrolytic substance appeared due to the pressure executed by the two samples in contact. However, this enabled the observation of titanium structure under the nanotubes layer. A difference can be noticed between titanium substrate observed under the nanotubes layer shown in Fig. 4b and titanium substrate shown under the nanotubes in Fig. 5b. A difference appears due to the intensive corrosion applied on the metal's surface. In this context it is acceptable that multi-layered nanotubes are created as a result of: (a) Formation of a thick titanium dioxide substrate on the interior sides of two samples positioned in contact, (b) stratification of titanium dioxide layer through intensive corrosive processes, (c) pores are scalloped at different levels, and (d) alternative processes developed on sample's surface due to accelerated molecules motion determine the buildup of nanostratified TiO₂ nanotubes. The phenomenon depends on factors such as: ions transport, ionic concentration gradient, current intensity, time of anodizing, samples pressure when in contact and mainly the inter-electrode distance. The result of all mentioned are the multi-layered titanium dioxide nanotubes created on pure titanium surface.

Variables that affect the electrolysis rate include voltage applied, electric current that flows, temperature, concentration, surface area of electrode covered by electrolyte solution and distance apart of the electrodes. Increased concentration of ions due to the increased anodized titanium surface intensifies the current and consequently the rate of electrolysis. Electrolytes that have more ions dissociated will have a higher rate of electrolysis. Increased surface area of the electrodes used increases the current and the rate of electrolysis. Also, decreased distance between the electrodes increases the current and the rate of electrolysis [64, 65].

5 Conclusions

The electrochemical anodizing is a dynamic process successfully used in materials surface manufacturing and particularly in titanium dioxide nanotubes synthesis. During the electrolysis many changes take place in the electrochemical cell, having as result the formation of different structures on the anodized surface.

Within this study multi-layered TiO₂ nanotubes were obtained through the electrochemical anodizing method. The multi-layered structure appeared after simultaneously anodizing two titanium plates in contact, both clipped to an

anodic wire and mounted in parallel with a graphite cathode. Factors such as the released cations, ions transfer and concentration gradient, as well as forces acting on samples' surface create the proper electrochemical environment for the formation of multi-layered TiO₂ nanotubes. The partial separation of bottom and surface layers of nanotubes can be done through ultrasonication and enables the observation of the stratified nano-architecture.

According to Nerst diffusion layer theory, the value of the limiting current density into the electrochemical cell may be increased by increasing the bulk ions concentration. In this case the current intensity and as a consequence all processes taking place in the electrochemical cell are intensified due to the existence of two titanium samples working as anode; the two specimens enable the release of a multiplied number of cations, therefore influencing the ionic concentration gradient in the electrolyte.

Important aspects in the synthesis of multi-layered TiO₂ nanotubes through electrochemical oxidation are the matter's diffusion and transport during electrolysis and these phenomena can be explained through First and Second Fick's laws. In this experimental work, the flow of mass is related to the electrolyte density and to ions speed, but particularly in the case of two simultaneously anodized samples it has to do with the reciprocal pressures executed by the two specimens in contact and its time dependence. Transfer and alternation of corrosive or other electrochemical phenomena together with continues molecules motion lead to the formation of TiO₂ nanotubes assembled on different height levels. For the synthesis of such nano-structures, a minimal distance between two titanium samples both clipped to the positive terminal of the cell is necessary.

As future issues, measurements related to nanotubes number of layers, nanotubes height in each layer, as well as a deeper understanding of the involved electrochemical phenomena and the application of the presented method to other materials would certify the possibility of creating multi-layered nano-structures on metals.

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